# Homework # 4: 3.13, 3.22 b, d, 3.23, 3.26

**3.13** For the reaction

$$pyruvic\ acid(l) \rightarrow acetaldehyde(g) + CO_2(g)$$

*a)* Determine $\Delta G^\circ_{298,\,rxn}$

**Solution**

Since this reaction takes place at STP, we can use the data in the tables at the back of the book.

$$\begin{aligned}
\Delta G^\circ_{298,\,rxn} &= \Sigma\Delta G^\circ_{298,\,products} - \Sigma\Delta G^\circ_{298,\,reactants} \\
&= \Delta G^\circ_{298,\,acetaldehyde} + \Delta G^\circ_{298,\,CO_2} - \Delta G^\circ_{298,\,pyruvic\ acid} \\
&= -133.30kJ/mol - 394.359kJ/mol - -463.38kJ/mol \\
&= -64.28kJ/mol
\end{aligned}$$

*b)* Determine $\Delta G$ at 298 K and 100 atm.

**Solution**

This reaction does not take place at STP. Therefore, the data in the back of the book cannot be used indiscriminately. Recall that, in differential form $dG = VdP - SdT$. We are interested in finding the change in G with a change in P, so we will look at the differential change in G which would be introduced by a small change in P, keeping temperature constant. An easy way to remember this is to imagine that we are dividing the differential form of $dG$ above by $dP$. This is not correct mathematical terminology, but it will give you the right answer. Evaluating this, we find:

$$\begin{aligned}
\left(\frac{\partial G}{\partial P}\right)_T &= V\left(\frac{\partial P}{\partial P}\right)_T - S\left(\frac{\partial T}{\partial P}\right)_T \qquad (1) \\
&= V
\end{aligned}$$

The second line follows from the first line since $\left(\frac{\partial P}{\partial P}\right)_T = 1$ and $\left(\frac{\partial T}{\partial P}\right)_T = 0$. You can determine those last two things just by taking derivatives–the derivative of $P$ with respect to $P$ is 1, and the derivative of $T$, where $T$ is held constant, with respect to $P$ is 0.

This relationship tells us how $G$ changes when pressure changes, which is what we want to know. In fact,

$$\int_{p_1}^{p_2}\left(\frac{\partial \Delta G}{\partial P}\right)_T d\,p = \Delta G(p_2) - \Delta G(p_1)$$

Here we have applied the Fundamental Theorem of Calculus: an integral essentially "undoes" a derivative. Now we can also evaluate this integral by plugging in our result from (1), and by using the ideal gas volume for V:

$$\begin{aligned}
\int_{p_1}^{p_2}\left(\frac{\partial \Delta G}{\partial P}\right)_T d\,p &= \int_{p_1}^{p_2}\Delta V dP \\
&= \int_{p_1}^{p_2}\frac{\Delta(nRT)}{p}dP \\
&= \Delta n_{rxn}RT\ln\left(\frac{p_2}{p_1}\right)
\end{aligned}$$

Setting these two sides equal and solving for $\Delta G(p2)$ gives:

$$\Delta G(p_2) = \Delta G(p_1) + \Delta n_{rxn} RT \ln\left(\frac{p_2}{p_1}\right) \tag{2}$$

We have determined $\Delta G(p1)$ in part 13a) above, and 2 moles of gas are evolved by this reaction. Therefore,

$$\begin{aligned}
\Delta G(p_2) &= -64.28kJ/mol + (2moles)(8.314J/molK)(298K)ln\left(\frac{100\ atm}{1\ atm}\right) \\
&= -64.28kJ/mol + 22.84kJ/mol \\
&= -41.44kJ/mol
\end{aligned}$$

This is the answer. You could have arrived at this answer equally well by copying Equation(2) above out of the textbook (where it is equation 3.45). However, it would behoove you to understand the mathematics behind this answer. Make sure you are familiar and comfortable with what has been done above!

**3.22** *b)* Does a heat pump violate the laws of thermodynamics?

**Solution**

One statement of the second law of thermodynamics is that heat cannot spontaneously flow from a cold body to a hot body. For the heat pump in qestion, heat would be flowing from a hot body (the earth a few feet below ground level) to a cold body (the artic temperature house). There is no thermodynamic reason to reject this idea.

However, any patent lawyer should be advised that the inventor is wasting his time–this device already exists and is patented!

*d)* Does spontaneous unmixing of gases violate the laws of thermodynamics?

**Solution**

It is true that the gases have (partially) spontaneously unmixed. However, since the total volume of the system has increased, there are drastically more ways to arrange the molecules, and the total entropy of the system has increased.

**3.23** *a)* If liquid water freezes, what happens to entropy?

**Solution**

Entropy decreases, since ice has an ordered crystal structure but water does not.

*b)* If liquid water freezes at 0 $°C$, what happens to Gibbs free energy?

**Solution**

Freezing of ice at 1 atm and 0 $°C$ is a reversible process, therefore $\Delta G = 0$.

*c)* What about enthalpy?

**Solution**

Enthalpy decreases. You can see this two ways. First, this is occuring at constant pressure, and the system is losing heat. Since $q_p = \Delta H$ than $\Delta H < 0$. The second way to see this is as follows: $\Delta G = \Delta H - T\Delta S$ at constant temperature and pressure. Since $\Delta G = 0$, and $\Delta S < 0$, than we can determine that $\Delta H < 0$ as well.

**3.26** If the atmosphere is isentropic, determine the temperature of the atmosphere 10 km above the Earth where the pressure is 210 torr.

**Solution**

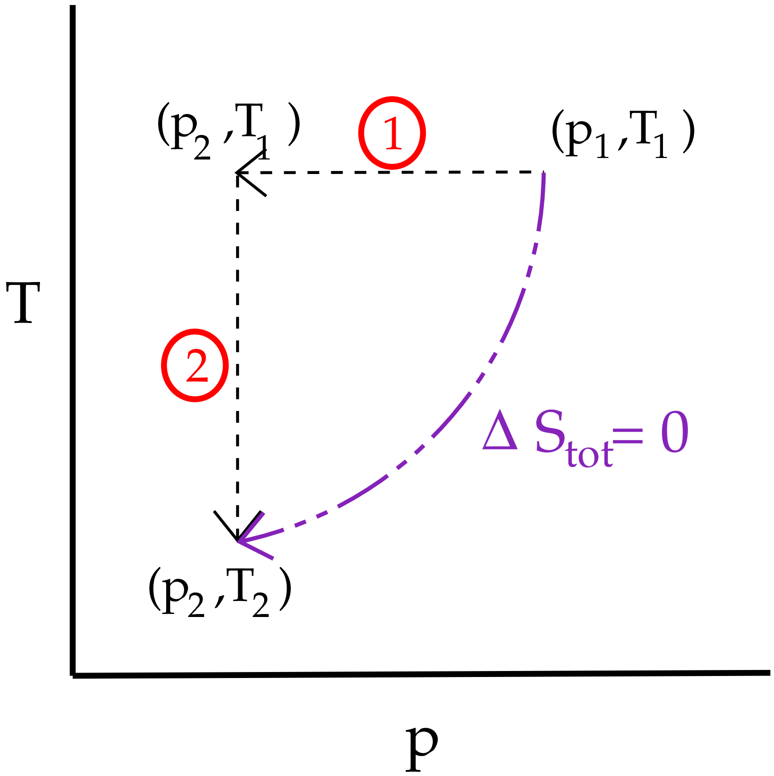


Figure 1: Possible paths to determine $\Delta S$

Since the atmosphere is approximately isentropic, this means that if $(p_1, T_1)$ and $(p_2, T_2)$ are temperatures and pressures which are realized in the earth's atmosphere at some height above the globe, than

$$\Delta S = S(p_2, T_2) - S(p_1, T_1) = 0$$

We can also determine $\Delta S$ for this change by examining two paths: the isothermal path (marked 1 on Fig. 1) and an isobaric path (marked 2 on Fig. 1). The respective $\Delta S$ for each path is as follows:

$$\begin{aligned}
\Delta S_{path\ 1} &= \int \frac{dq_{rev}}{T} \\
&= \frac{q_{rev}}{T} \qquad \text{since the path is isothermal} \\
&= \frac{RT ln(p_1/p_2)}{T} \qquad \text{for one mole of atmosphere} \\
&= R ln\left(\frac{p_1}{p_2}\right) \\
\Delta S_{path\ 2} &= \int \frac{dq_{rev}}{T} \\
&= \int \frac{C_p\, dT}{T} \qquad \text{since the path is isobaric} \\
&= C_p ln\left(\frac{T_2}{T_1}\right) \\
&= 7/2 R ln\left(\frac{T_2}{T_1}\right)
\end{aligned}$$

Since $\Delta S_{tot} = \Delta S_{path\ 1} + \Delta S_{path\ 2} = 0$, we can say

$$\begin{aligned}
-Rln\left(\frac{p_1}{p_2}\right) &= \frac{7}{2}Rln\left(\frac{T_2}{T_1}\right) \\
\frac{p_2}{p_1} &= \left(\frac{T_2}{T_1}\right)^{7/2} \\
T_2 &= \left(\frac{p_2}{p_1}\right)^{2/7} \times T_1 \\
&= \left(\frac{210\ torr}{760\ torr}\right)^{2/7} \times 298K \\
&= 206K = -67^{\circ}C
\end{aligned}$$

We are told that the actual temperature measured during rocket flights is -50 $^{\circ}C$. So our value is only off by around 7%.